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(54) **Photoresist materials**

(57) Resist materials comprise a novolac resin prepared from cresol and formalin wherein the formalin is used in excess to introduce a branched structure in the novolac resin, and a diazo compound chemically combined with the novolac resin. The resist materials may further comprise a dihydroxybenzene derivative. The molar ratio of cresol to formalin ranges from 1:1 to 1:4.

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novolac resin at phenolic hydroxyl groups thereof.

Intensive studies have revealed that when formalin is used in excess upon preparation of a novolac resin to introduce a branched structure into the resin, the developing speed with a developer (an alkaline solution) can be increased, resulting in an improvement of resist sensitivity and gamma characteristic, so that when a photosensitizing agent and the novolac resin are chemically combined, satisfactory sensitivity is ensured using a small amount of the photosensitizer, thus leading to an improved light transmittance, thereby improving the resist shape properties.

Moreover, when dihydroxybenzene derivatives are contained in the resin, the resist can be more clearly held in a rectangular form in section.

According to the present invention there is also provided a resist material which comprises a novolac resin which is prepared from cresol and formalin at a molar ratio of 1:1 to 1:4 to have a branched structure therein and containing a dihydroxybenzene derivative, and a diazo compound chemically combined with said novolac resin at phenolic hydroxyl groups thereof.

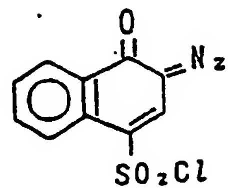
According to one embodiment of the invention, there is provided a resist material which comprises a novolac resin prepared from cresol and formalin at a molar ratio of 1:1 to 1:4, and a diazo compound chemically combined with the novolac resin at phenolic hydroxyl groups thereof.

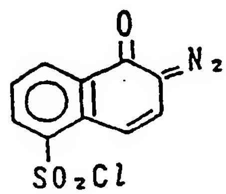
According to another embodiment of the invention, there is also provided a resist material which comprises a novolac resin prepared from cresol and formalin at a molar ratio of 1:1 to 1:4 and containing a dihydroxybenzene derivative, and a diazo compound chemically combined with the novolac resin at phenolic hydroxyl groups thereof.

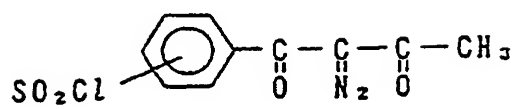
The invention will now be further described by way of example with reference to the sole figure which is a structural formula showing a branched structure of a novolac resin according to the invention.

Embodiments of resist material according to the invention comprise a major proportion of a novolac resin prepared from cresol and formalin. For the preparation, the molar ratio between cresol and formalin is controlled such that formalin is in excess, whereby a branched structure is introduced into the resin.

Accordingly, the cresol/formalin ratio at the time of the



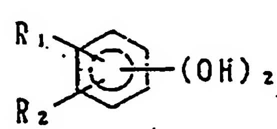




When the diazo compound has, for example an $-SO_2Cl$ group, the chemical combination is accomplished through the sulphonic ester bond with the hydroxyl group of the novolac resin.

The amount of the diazo compound should preferably be in the range of 3 to 30 wt% of the novolac resin. If the amount of the diazo compound is smaller, satisfactory strength cannot be obtained. On the contrary, larger amounts lead to a lowering of light transmittance, resulting in a lowering of sensitivity.

In another embodiment of the invention, the novolac resin further comprises dihydroxybenzene derivatives. The dihydroxybenzene derivative is represented by the following formula



The invention will not be further described by way of examples.

Example 1

Preparation of Novolac Resins

25 g of meta-cresol, 24.3 g of formalin and 180 mg of oxalic acid were weighed and heated and agitated in ethyl cellosolve acetate for reaction at 120°C for 5 hours.

The resultant product was re-precipitated in water to remove unreacted formalin therefrom, followed by drying under reduced pressure. The resultant resin had a weight average molecular weight of about 2000.

In the above reaction, the molar ratio (cresol/formalin) was 1/1.3. The amounts were changed to prepare novolac resins with cresol/formalin ratios of 1/1, 1/1.1, 1/1.5, 1/2 and 1/3. These had a weight average molecular weight of about 2000 by controlling the polymerization time.

The thus prepared novolac resins were confirmed through NMR spectra with respect to the branching at about 1 per the number of bonds of 10 for the molar ratio of 1/1.3, about 1 per the number of bonds of 5 for the molar ratio of 1/1.5, and about 1 per the number of bonds of 3 for the molar ratio of 1/2.

Introduction of Diazo Compound

9 g of the respective novolac resins prepared above and 0.63 g of naphthoquinonediazido-4-sulphonyl chloride (7 % by weight of the resin) were dissolved in dioxane, in which 0.33 ml of triethylamine was dropped to cause naphthoquinonediazido-4-sulphonyl chloride to ester bond with the novolac resin.

The resultant products were each re-precipitated in a hydrochloric acid aqueous solution to remove the amine salt therefrom.

Finally, the reaction product was dissolved in ethyl cellosolve acetate, followed by filtration through a filter with a pore size of 0.2μ m to provide a photoresist.

The respective resists had a gamma value, sensitivity and resin dissolution rate indicated in Table 1 below.

between cresol and formalin results in an increase of the dissolution rate, with the result that the resist sensitivity is improved with improved shape properties.

For comparison, a novolac resist having high resolving power was selected from commercial resists and subjected to similar measurements, with the result that the resist sensitivity was in the range of 200 to 460 mJ/cm^2, the resolving power was in the range of 0.4 to 0.5 μm and the side wall angle was in the range of 60 to 70°. Thus, the resist sensitivity, resolving powder and the shape of the resist were found to be significantly poorer than those of the resist materials according to the invention.

Example 2

Preparation of Resin

25.8 g (0.239 moles) of meta-cresol, 1.38 g (0.0126 moles = about 5 mole%) of hydroquinone, 30.6 g of formalin and 193 mg of oxalic acid were weighed and heated and agitated in ethyl cellosolve acetate for reaction at 120°C for 3 hours.

The resultant product was re-precipitated in water to remove unreacted formalin therefrom, followed by drying under reduced pressure. The resultant resin had a weight average molecular weight of about 2300.

Similarly, a novolac resin having 20 mole% of hydroquinone was prepared.

In these novolac resins, the copolymerization of hydroquinone was confirmed through ^{1}H-NMR. The molar ratios between cresol and formalin in the resins were approximately 1:1.5 for both cases.

Introduction of Diazo Compound

9 g of the respective novolac resins prepared above and 0.72 g of naphthoquinonediazido-4-sulphonyl chloride (8 % by weight of the resin) were dissolved in dioxane, in which 0.38 ml of triethylamine was dropped to cause naphthoquinonediazido-4-sulphonyl chloride to ester bond with the novolac resin.

The resultant product was re-precipitated in a hydrochloric acid aqueous solution to remove the amine salt therefrom.

Finally, the reaction product was dissolved in propylene glycol methyl ether acetate, followed by filtration through a filter with a pore size of 0.2 μm to provide a photoresist.

Formation of Pattern

spin coated in a thickness of 1 μm on a silicon substrate and subjected to measurement of a developing rate by immersion in a liquid developer. The developing time was 60 seconds and the concentration of the developer was changed.

The developers used were tetraethylammonium hydroxide (TMAH) aqueous solutions with concentrations of 2 wt%, 1 wt%, 0.7 wt%, 0.5 wt%, 0.3 wt% and 0.1 wt%, respectively.

During the development, it was observed that the developing rates were different in the surface and in the inside of the resist. These were named as a surface sparingly soluble layer and a bulk layer. The ratio in the developing rate between the surface sparingly soluble layer and the bulk layer (the surface sparingly soluble layer/the bulk layer), an etching rate of the bulk layer and a resist side wall angle were measured. The results are shown in Table 4.

Table 4

Concentration of Developer (wt%)	Ratio in Developing Rate	Etching Rate of Bulk Layer (μm/second)	Resist Side Wall Angle
2	1/1	5	75°
1	1/2	3	80°
0.7	1/5	1	83°
0.5	1/10	1	85°
0.3	1/15	0.5	85°
0.1	no dissolved	-0.1	-

From the above experiment, it was confirmed that the resist pattern form became better at a slower developing rate of the sparingly soluble layer relative to the bulk layer.

Usually, the resist thickness should be 0.7 to 1 μm and the developing time should be approximately 60 seconds. The concentration of the liquid developer should preferably be approximately 0.5 to 0.7 wt%.

As will become apparent from the foregoing, the resist materials of the invention have a branched structure by using an excess of formalin at the time of preparation of the novolac resin, so that a dissolution rate in an alkali aqueous solution can be substantially

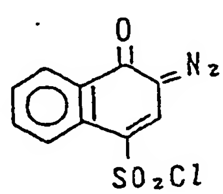
CLAIMS

1. A resist material which comprises a novolac resin which is prepared from cresol and formalin at a molar ratio of 1:1 to 1:4 to have a branched structure therein, and a diazo compound chemically combined with said novolac resin at phenolic hydroxyl groups thereof.

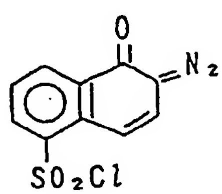
2. Resist material according to claim 1 wherein said molar ratio is in the range of from 1:1.5 to 1:2.

3. Resist material according to claim 1 wherein said diazo compound has a functional group capable of chemical combination with the phenolic hydroxyl groups of said novolac resin.

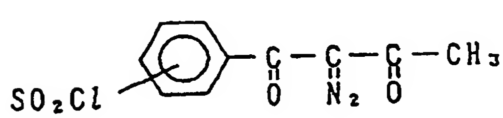
4. Resist material according to claim 3 wherein said diazo compound is of the following formula (1), (2) or (3)



(1)



(2)



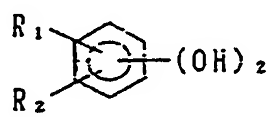
(3)

5. Resist material according to claim 1 wherein said diazo compound is used in an amount of from 3 to 20 wt% of said novolac resin.

11. Resist material according to claim 6 wherein said dihydroxybenzene derivative is contained in said novolac resin by mixing of said derivative with said novolac.

12. Resist material according to claim 6 wherein said dihydroxybenzene derivative is contained in said novolac resin in copolymerizing said derivative with the cresol and formalin.

13. Resist material according to claim 6 wherein said dihydroxybenzene derivative is of the following formula



wherein R_1 and R_2, respectively, represent hydrogen, chlorine, an alkyl group or an alkoxy group.

14. Resist material according to claim 6 wherein said dihydroxybenzene derivative is contained in an amount of from 2 to 30 wt% based on the novolac resin.

15. A resist material substantially as hereinbefore described with reference to any one of the Examples.

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